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Transient optical studies of charge recombination dynamics in a polymer/fullerene composite at room temperature

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The recombination kinetics of photogenerated charge carriers in a composite of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1-4-phenylene vinylene], (MDMO-PPV) and the functionalised fullerene 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C_{60} are investigated at room temperature by transient absorption spectroscopy. The decay dynamics of positively charged MDMO-PPV polarons were found to be either monophasic or biphasic, depending upon the laser excitation density employed. The slower, power law, decay phase (100 ns–10 ms) is attributed to recombination dynamics of localized polarons, while the fast decay component (<20 ns) is attributed to recombination of relatively mobile polarons observed when the density of localized states is exceeded by the density of photogenerated polarons ($\sim 10^{17} \text{ cm}^{-3}$). The implications of these observations are discussed in relation to polymer/ C_{60} photovoltaic cells. © 2002 American Institute of Physics.
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The optical and electronic properties of organic molecular and polymer films are attracting extensive interest for applications in organic light emitting diodes and solar cells.¹ Photovoltaic device function^{2,3} has been achieved by blending organic materials of suitable electron affinities and ionization potentials. Blends of conjugated polymers and fullerenes (C_{60})^{3,4} have, in particular, achieved quantum yields of photoinduced charge generation close to 100%.⁴ The function of such films is based upon an electron transfer from the photogenerated excited state of the conjugated polymer to fullerene acceptors. This charge separation results in a metastable charge separated state with the electron on the fullerene molecule and a positive charge (polaron) delocalized on the polymer backbone.

While the dynamics of the charge separation reaction in such organic blends have received significant attention to date^{3,5–7} the reverse charge recombination reaction has been less widely studied. Nevertheless kinetic competition between this recombination reaction and charge collection by device electrodes is likely to be a key factor which may limit device performance.^{8,9} The blending of the two organic components on a length scale smaller than the exciton diffusion length (typically 10 nm) is essential for efficient charge separation; however, this intimate blending may also have the detrimental effect of facilitating the unwanted charge recombination reaction.

In this letter we employ transient absorption spectroscopy to study the recombination dynamics of a polyphenylene-vinylene (PPV)/ C_{60} blend on nanosecond to millisecond time scales at room temperature. Previous studies

have largely employed frequency domain techniques at low temperatures, with a chopped excitation beam at frequencies up to ~ 10 kHz [often referred to as “photoinduced absorption” (PIA) studies]. Such studies have, for a broad range of polymer/ C_{60} films, reported the observation of photoinduced polaron absorption on millisecond time scales. In contrast to frequency domain measurements, time domain transient absorption studies (TAS) employing pulsed laser excitation have typically reported recombination dynamics in polymer/ C_{60} films on the picosecond and nanosecond time scales.^{7–10}

Our previous studies of dye sensitized, nanocrystalline solar cells have demonstrated that the excitation density employed strongly influences the observed recombination dynamics.¹¹ The influence of excitation density has however not been consistently addressed in previous TAS and PIA studies of polymer/ C_{60} blends. In this letter, we therefore conduct a time resolved study over two orders of magnitude in excitation intensity, and demonstrate that recombination dynamics in polymer/ C_{60} blends are strongly dependent upon the excitation intensity employed.

In this work we studied blends of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1-4-phenylene vinylene] (MDMO-PPV) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C_{60} (PCBM) at room temperature. Blend compositions of 1:2 and 1:4 (w/w) were studied; these two compositions were found to give indistinguishable recombination dynamics. 100-nm-thick films were deposited by spin coating from chlorobenzene solution onto glass slides. Such films have been previously shown to yield photovoltaic devices with energy conversion efficiencies of up to 2.5%.^{4,12} Film optical density at 500 nm was 0.3–0.5. Frequency domain PIA experiments were conducted at 100 K as reported previously.¹³ Nanosecond to millisecond TAS employed 500

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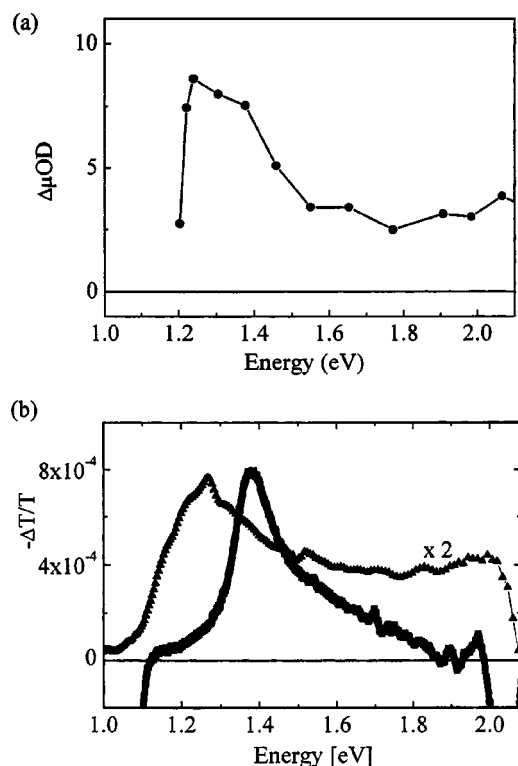


FIG. 1. (a) Transient absorption spectra of a MDMO-PPV/PCBM blend obtained 125 μ s after excitation at 500 nm ($80 \mu\text{J cm}^{-2}$ per pulse), $T = 296$ K; (b) frequency domain photoinduced absorption spectra of (—■—) pristine MDMO-PPV and (---▲---) of a MDMO-PPV/PCBM blend ($\times 2$) employing excitation at 488 nm with 40 mW and 132 Hz modulation, $T = 100$ K. Note that ΔOD and $-\Delta T/T$ are related by $\Delta OD = 1/2.303 (-\Delta T/T)$.

nm (2.48 eV) excitation pulses (frequency 4 Hz, duration < 1 ns). The change in the sample transmission was monitored using either a 830 nm (1.49 eV) laser diode for timescales up to 300 ns or a tungsten lamp with monochromators before and after the sample (probe intensity $\sim 1 \text{ mW cm}^{-2}$) for longer time scales. Data on each time scale resulted from averaging 100–1000 laser shots. No degradation of the samples, stored and measured under argon, was observed during any of the experiments reported here. Particular care was taken to subtract contributions from laser scatter and sample emission from the data.

We consider first the assignment of the transient optical signal. Pulsed laser excitation of the MDMO-PPV/PCBM resulted in a broad, long-lived photoinduced absorption increase in the red/near-infrared. The transient spectrum of this TAS signal measured at 296 K at a time delay of 125 μ s, is displayed in Fig. 1(a). As a comparison, Figs. 1(b) and 1(c) show the frequency domain photoinduced absorption spectra of a pristine MDMO-PPV film and the MDMO-PPV/PCBM blend collected using 132 Hz modulation at 100 K. In the case of the pristine MDMO-PPV film [Fig. 1(b), —■—], this PIA spectrum exhibits a single maximum at 1.38 eV previously assigned to absorption of the MDMO-PPV triplet state.^{7,9,13} In contrast, the PIA spectrum for the MDMO-PPV/PCBM blend [Fig. 1(b), -▲-] exhibits a broader absorption increase with two maxima at 1.27 and 2.0 eV previously assigned to absorption of MDMO-PPV positive polarons.^{6,14} Comparison of the transient absorption spectrum of the MDMO-PPV/PCBM film shown in Fig. 1(a) with the two

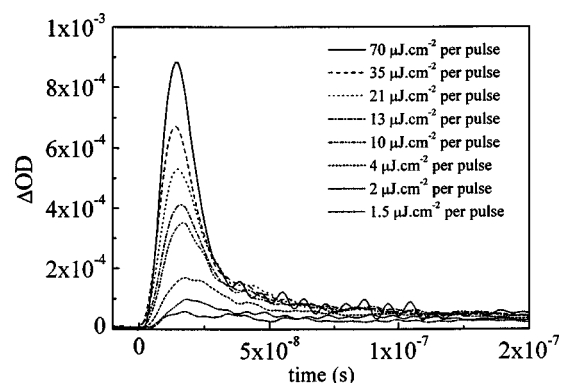


FIG. 2. Transient absorption kinetics observed for the MDMO-PPV/PCBM blend on the nanosecond time scale using different excitation densities. The excitation densities ranged between 1.5 and $70 \mu\text{J cm}^{-2}$ per pulse. The decay is assigned to charge recombination between electrons in the fullerene and the positive polarons in the conjugated polymer. The sample was excited at 500 nm at a repetition rate of 4 Hz and probed using a laser diode at 830 nm, $T = 296$ K.

PIA spectra in Fig. 1(b) clearly shows that the transient spectrum closely matches that observed in the frequency domain PIA studies of the blend, and is therefore also assigned to positive MDMO-PPV polarons generated by photoinduced electron transfer from MDMO-PPV to PCBM.

We now consider the decay dynamics of the MDMO-PPV polaron transient absorption signal. Figure 2 shows the kinetics for the MDMO-PPV/PCBM blend on the nanosecond time scale using excitation densities ranging from 1.5 to $70 \mu\text{J cm}^{-2}$ per pulse ($4\text{--}180 \times 10^{12}$ photons cm^{-2} per pulse). It is apparent that the decay dynamics are strongly dependent upon laser intensity. At high laser intensities, they are dominated by a fast, instrument response limited (~ 20 ns) decay phase. The amplitude of this fast phase is excitation density dependent and reduces in amplitude by at least 20-fold over the range of excitation densities employed. In contrast, as shown in Fig. 3 the longer timescale data is relatively insensitive to laser power, e.g., the signal in the 50–100 ns time window reducing in amplitude by only $\sim 50\%$ over the same range. At the lowest excitation power employed, ($1.5 \mu\text{J cm}^{-2}$ per pulse), the instrument response limited (< 20 ns) decay is negligible, and the slower timescale dynamics dominate the decay.

In Fig. 4 we show an extension of our data to millisecond time scales on log/log axes. The long lived residual sig-

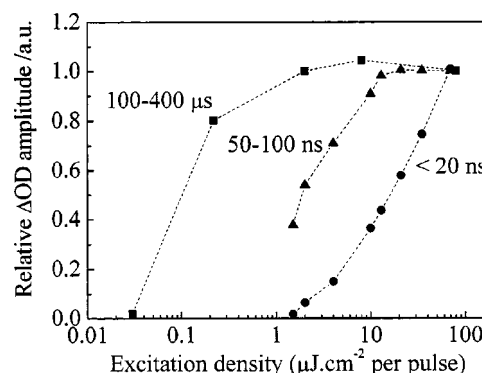


FIG. 3. Relative amplitude of the transient absorption signal for the MDMO-PPV/PCBM blend as a function of laser excitation power: (—●—) amplitude of instrument response (~ 20 ns) limited decay; (—▲—) transient signal at 50–100 ns; (—■—) transient signal at 100–400 μ s. Other experimental conditions as for Fig. 2.

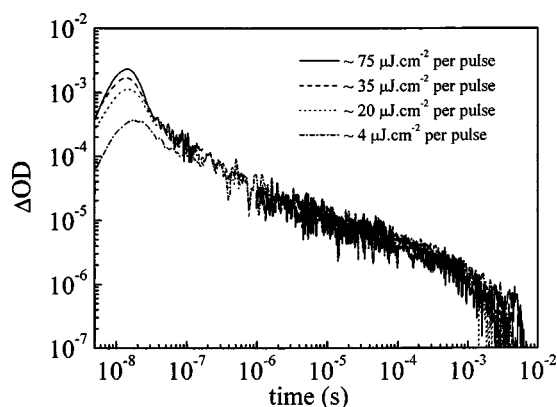


FIG. 4. Transient absorption decay kinetics observed for the MDMO-PPV/PCBM blend on the nanosecond to millisecond time scales. Transient absorption data for time delays >300 ns collected at 940 nm. Other experimental conditions as for Fig. 2.

nal observed in the nanosecond data persists up to milliseconds. As observed in Fig. 2, at longer time delays the transient signal becomes increasingly less sensitive to the excitation intensity employed. Indeed, for time delays greater than ~ 300 ns, the transient signal is independent of excitation density for excitation densities employed down to $<1.5 \mu\text{J cm}^{-2}$ per pulse [for excitation densities $<1 \mu\text{J cm}^{-2}$ per pulse, the amplitude of this long lived signal starts to become smaller, as shown in Fig. 3 (---)]. It is furthermore apparent that the slow time scale transient decay dynamics exhibits a power law type behavior

$$\Delta O.D. \propto t^{-\alpha}. \quad (1)$$

From the gradient of the decays, we obtain $\alpha = 0.4 \pm 0.02$.

We conclude from the data shown in Figs. 2 and 4 that the decay dynamics of MDMO-PPV positive polarons in photoexcited MDMO-PPV/PCBM blends can be approximated by a fast (instrument response limited, <20 ns) component dependent upon excitation density and a slow component that exhibits a power law decay and is independent of excitation density down to $\sim 1 \mu\text{J cm}^{-2}$ per pulse.

The power law type recombination dynamics observed for time delays >300 ns are indicative of localized carriers, as has previously been suggested by Meskers *et al.*⁸ These dynamics are consistent with pico- to nanosecond relaxation of the charge carriers down to the lowest energy states of the inhomogeneously broadened density of states typical of such materials, below the mobility edge for the material. The presence of localized states is furthermore consistent with transient photoconductivity and LESR studies of PPV/C₆₀ films.¹⁵ The saturation of the amplitude of the power law decay observed here for excitation intensities $>1 \mu\text{J cm}^{-2}$ per pulse is consistent with saturation of the density of available localized states. Taking account of the sample absorption at the excitation wavelength (transmission $\sim 40\%$) and assuming a unity quantum yield of polaron formation per absorbed photon,⁴ this threshold excitation density corresponds to $\sim 10^{17}$ photogenerated polarons cm^{-3} . This calculation neglects any charge recombination occurring on time scales $\ll 20$ ns, in agreement with the data shown in Fig. 2 for the low excitation densities employed. Following from this analysis, the fast, <20 ns decay phase observed for laser intensities $>1.5 \mu\text{J cm}^{-2}$ per pulse can be assigned to rela-

tively mobile polarons present when the density of photogenerated polarons exceeds the density of localized states below the PPVs mobility edge. We note that the laser power dependence we observe is not consistent with the assignment of the <20 ns phase to geminate recombination.⁸

We conclude by noting that the recombination dynamics in photovoltaic device fabricated from polymer/C₆₀ cells under solar illumination can be expected to be dominated by the slower decay phase we report here. The rate of carrier generation under steady state solar illumination is $\sim 3 \times 10^{16}$ polarons $\text{s}^{-1} \text{cm}^{-2}$ (estimated from the optimum short circuit current of 5 mA cm^{-2}).⁴ Given the ns- μs recombination dynamics reported here for localized polarons, the polaron density generated by steady state solar illumination is not expected to exceed the estimated density of localized states ($\sim 10^{17} \text{ cm}^{-3}$), and the recombination dynamics will most probably be dominated by the slow, power law decay we assign to recombination dynamics of localized MDMO-PPV polarons with C₆₀ anions. More quantitative analysis of these recombination dynamics and their competition with carrier collection dynamics in complete photovoltaic cells will be presented elsewhere.¹⁶

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